Lithium-Metal Anodes: Problems and Multiple Solutions Based on Electrolytes, Hosts, and Protective Layers

Ji-Guang Zhang (PI), Wu Xu, Jun Liu

Pacific Northwest National Laboratory

2018 DOE Vehicle Technologies Program Review
June 18-21, 2018

This presentation does not contain any proprietary, confidential, or otherwise restricted information

Project ID #: bat362

Overview

Timeline

- Project start date: Oct. 2016
- Project end date: Sep. 2021
- Percent complete: 30%

Budget

- Total project funding $50M
  - DOE share 100%
- Funding received in FY17: $10M
- Funding received in FY18: $10M

Barriers

- Low Coulombic efficiency
- Li dendrite growth
- Large volume change

Partners

- Pacific Northwest National Laboratory
- Stanford University
- SLAC
- Idaho National Laboratory
- University of Washington
- University of California at San Diego
- UT Texas

Relevance/Objectives

- Develop stable electrolytes to improve the Coulombic efficiency of Li metal anode
- Develop ex situ formed artificial SEI layer to protect Li metal against dendrite growth
- Develop efficient host for Li metal to minimize volume change of Li based anode
- Enable operation of thin Li metal in lean electrolyte conditions
- Enable high efficiency and safe utilization of Li metal anode for high energy density Li metal batteries required for long range EV applications

BATTERY 500 CONSORTIUM

Pacific Northwest NATIONAL LABORATORY

Milestones

- Investigate methods to extend the cycling and stability of Li metal pouch cells.. (Dec-31, 2017). **Completed**
- Establish the high Ni NMC coin cell properties using the materials synthesized by the team and supplied by other sources (Mar-31, 2018). **Completed**
- Provide feedback on characterization of the new materials and concepts by the characterization team. (Jun-30, 2018). **On track**
- Develop and implement methods to improve and understand cycle and calendar life limitations of pouch cells. (Sep-30, 2018). **On track**

Approach

Battery500 Solutions

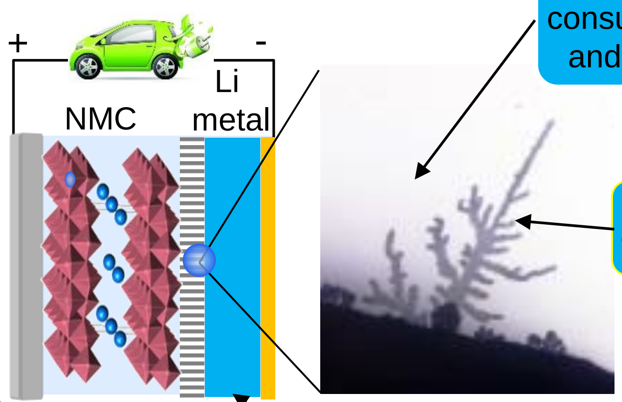
Stable Electrolyte (PNNL)

- High concentration electrolyte
- Localized High Concentration Electrolyte (LHCE)
- Non-flammable LHCE
- ≥300 Wh/kg Li metal pouch cells have been successfully fabricated and demonstrated >100 stable cycling.

Host:

- Form stable host for Li metal: Li-SiO composite (Stanford)
- Thin stable 3D conductive host without sacrificing the energy density (PNNL)

Challenges on Li metal anode



Simulation
Li metal batteries (UW)

Testing
Li metal batteries (INL)

Protection layer:

- Self-healing polymer (Stanford)
- Form stable artificial SEI layer via gas-phase reaction(Stanford)
- Selective deposition and stable encapsulation of lithium through heterogeneous seeded growth (Stanford)
- Li-methyl Carbonate Protection Layer (UCSD)
- Solid state electrolyte (UT Austin)

Characterization:

- Reveal the atomic structure of Li metal by cryo-electron microscopy (Stanford/UCSD)
- X-ray characterization (SLAC)

Technical Accomplishments

Localized high concentration electrolyte (LHCE) for high efficiency Li metal batteries

Limitations of HCE:

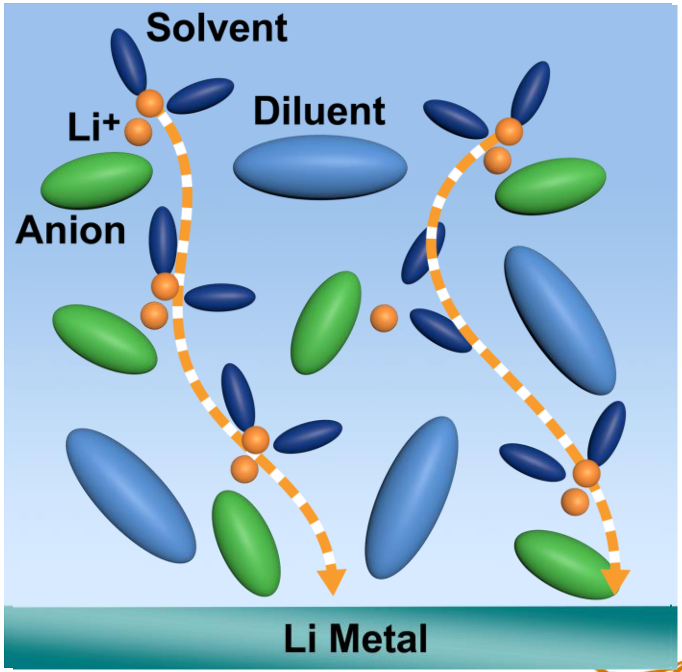
- High cost
- High viscosity
- Low conductivity

Advantages of LHCE:

- Retained all advantages of HCE
- Low cost
- Low viscosity
- High conductivity

Rational design of LHCE electrolyte:

a. A base solvent (DMC) with a high solvability of Li salt
b. A Li salt (LiFSI) stable with Li metal anode
c. A diluent (BTFE) with a very limited solvability of Li salt and fully mixable with base solvent
d. Li^+ will transports along the solvent/salts clusters with localized high salt concentration so advantages of HCE can be preserved.

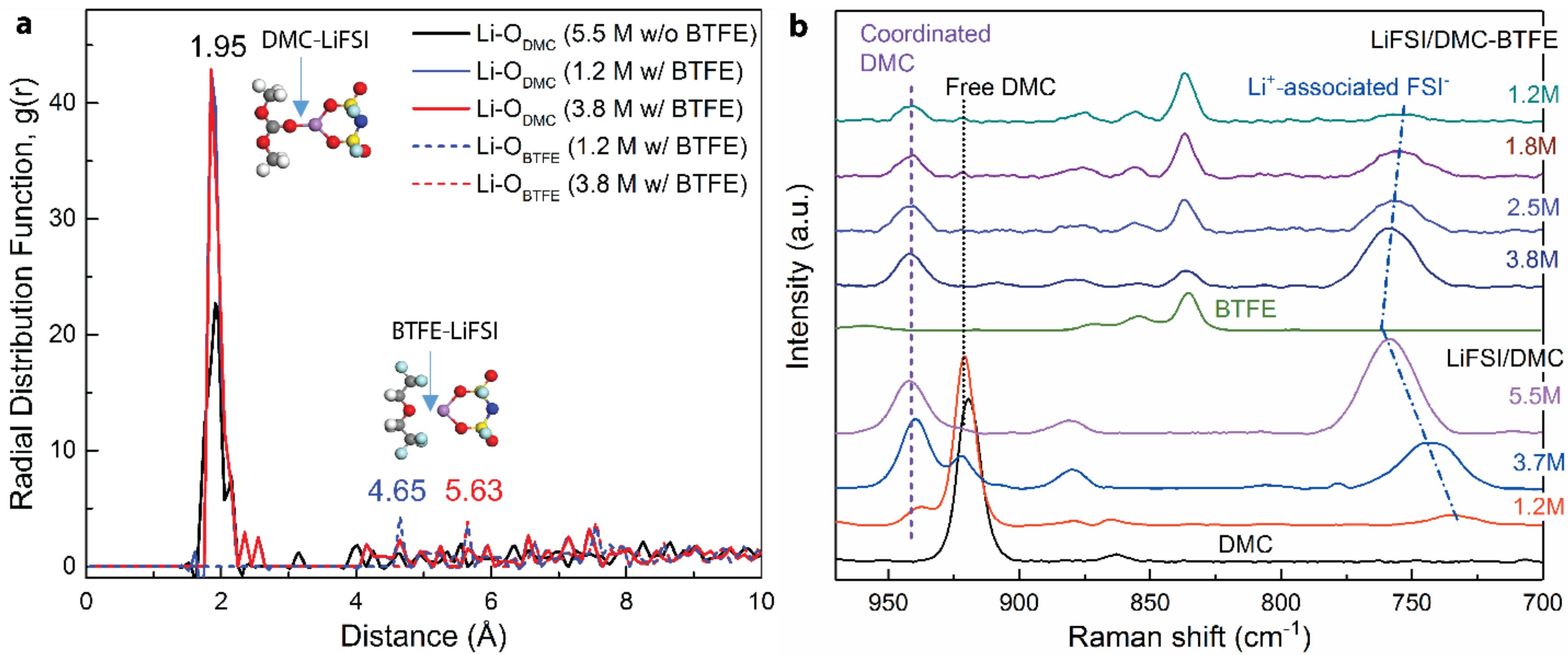


S. Chen and J-G.Zhang et al. *Adv. Mater.* **2018**, *30*, 1706102

Technical Accomplishments

Formation of localized high concentration clusters in molecular level

A typical example of LHCE: 1.2 M LiFSI in DMC:BTFE (1:2 by mole)



a. DMC-LiFSI has binding that is much stronger than BTFE-LiFSI binding
b. Addition of BTFE does not significantly affect the original LiFSI-DMC binding

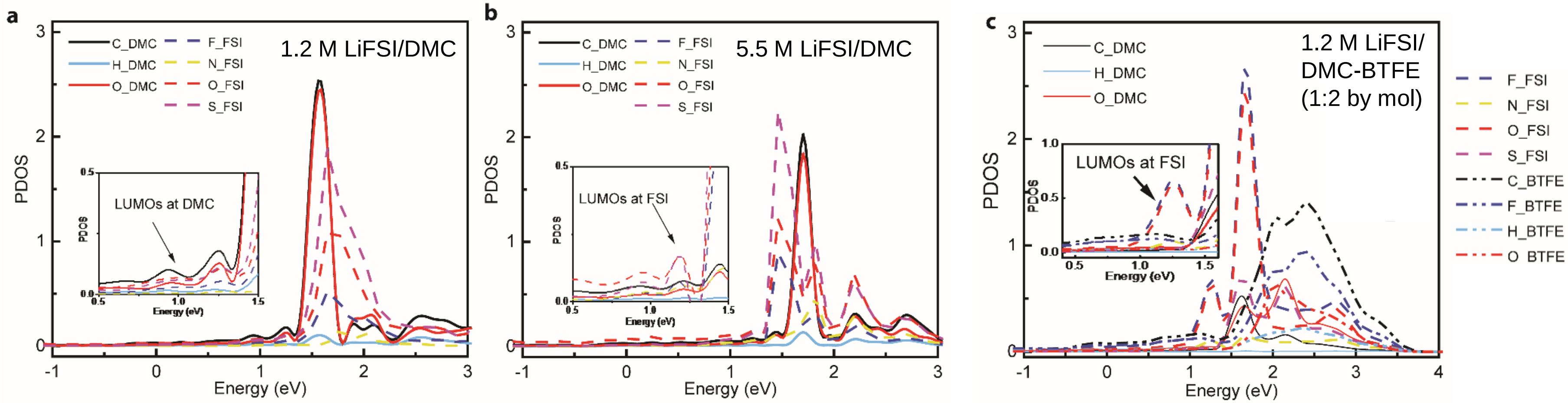
S. Chen and J-G.Zhang et al. *Adv. Mater.* **2018**, *30*, 1706102

BATTERY 500 CONSORTIUM

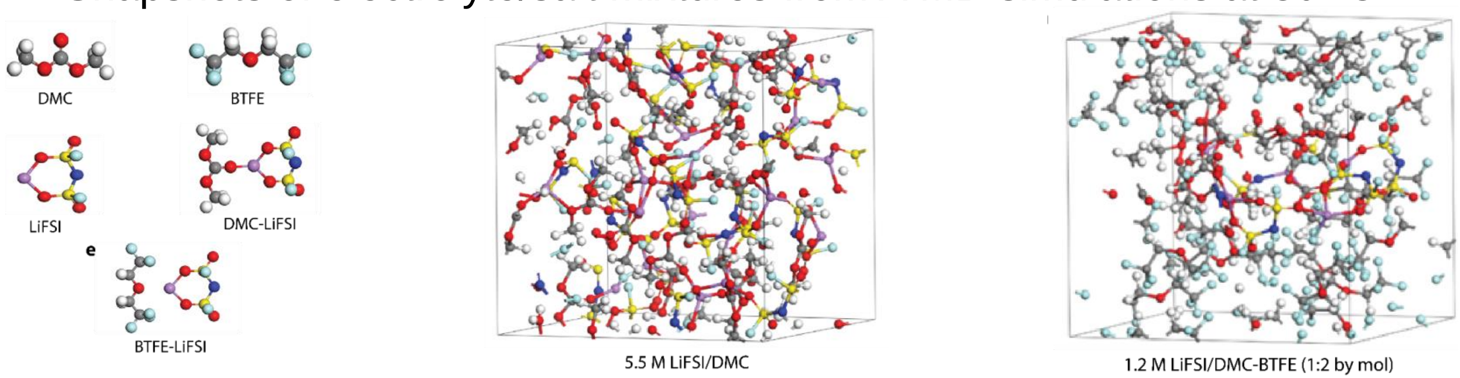
Pacific Northwest NATIONAL LABORATORY

Technical Accomplishments

Projected density of states (PDOS) of each atom on the Li anode surface in different electrolytes



Snapshots of electrolyte/salt mixtures from AIMD simulations at 30 °C



- ➢ LUMO energies of FSI anion in HCE and LHCE shift to lower than those of DMC solvent so salt will be decomposed first to form a LiF rich SEI to protect Li metal anode.
- ➢ All LiFSI salt molecules are closely coordinated with DMC instead of BTFE in the HCE and LHCEs.

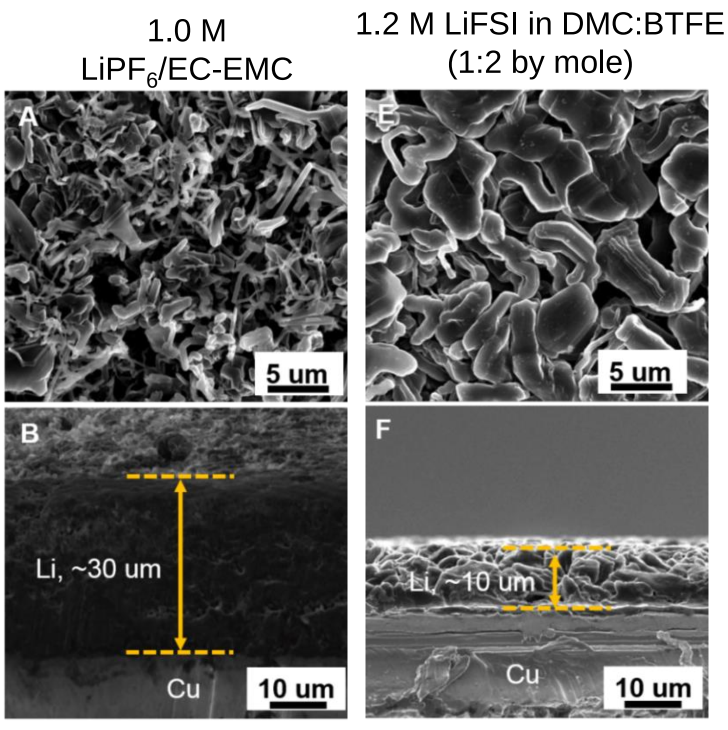
BATTERY 500 CONSORTIUM

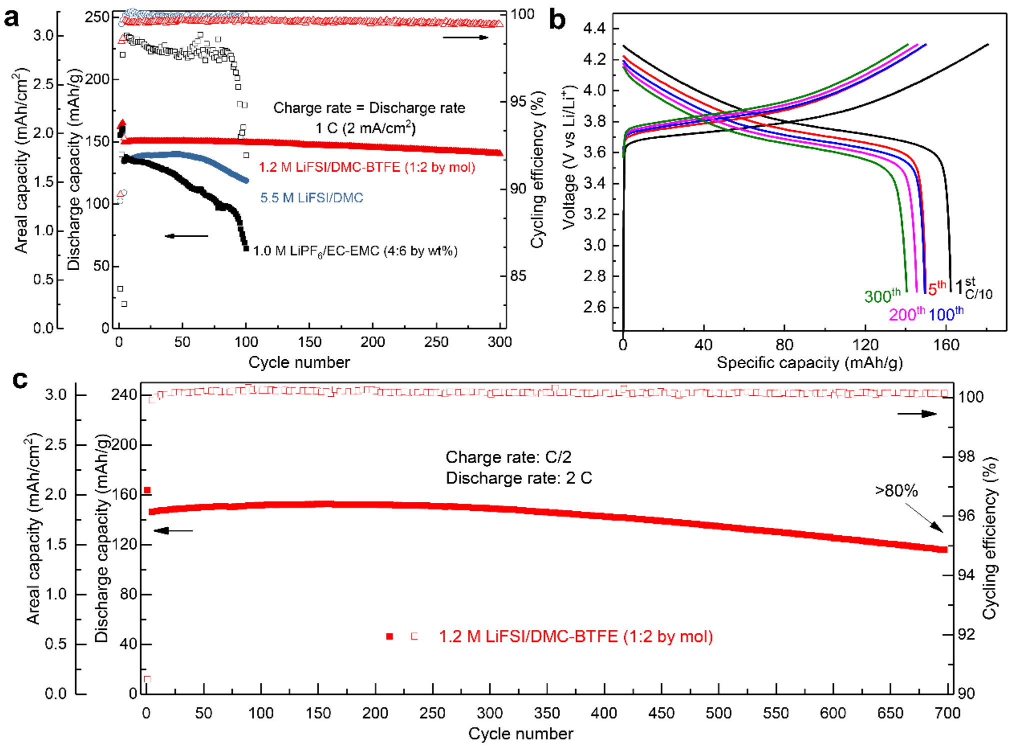
S. Chen and J-G.Zhang et al. *Adv. Mater.* **2018**, *30*, 1706102

Pacific Northwest NATIONAL LABORATORY

Technical Accomplishments

High performance Li metal batteries based on LHCE





Highly packed granule Li particles (~10 μm) formed in LHCE electrolyte exhibits small surface area and will not penetrate separator

Stable cycling of Li/NMC batteries with LHCE (>80% capacity retention after 700 cycles at a high current density of 2.0 mA/cm²)

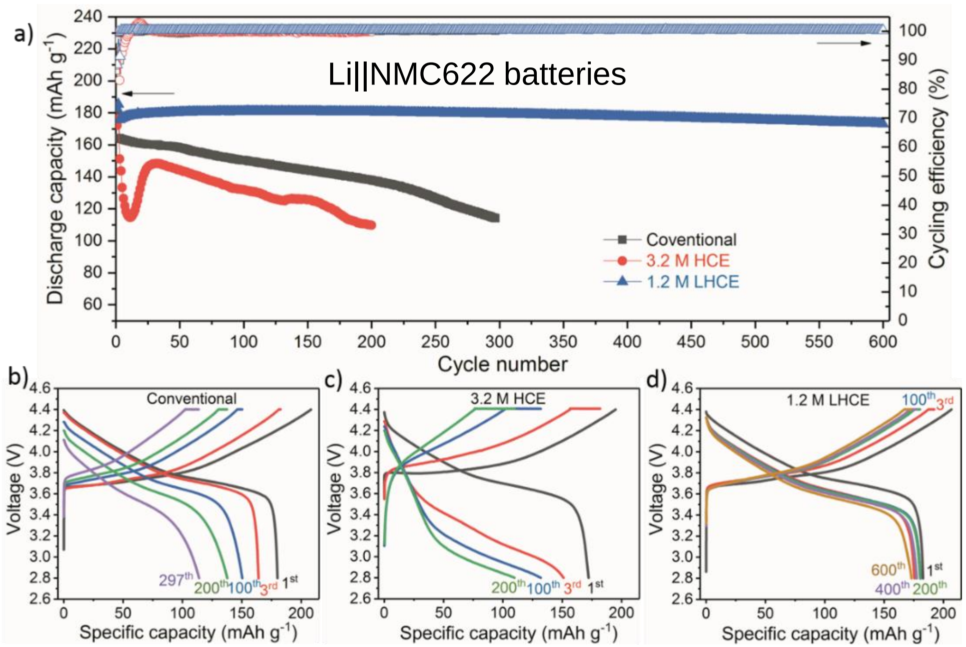
S. Chen and J-G.Zhang et al. *Adv. Mater.* **2018**, *30*, 1706102

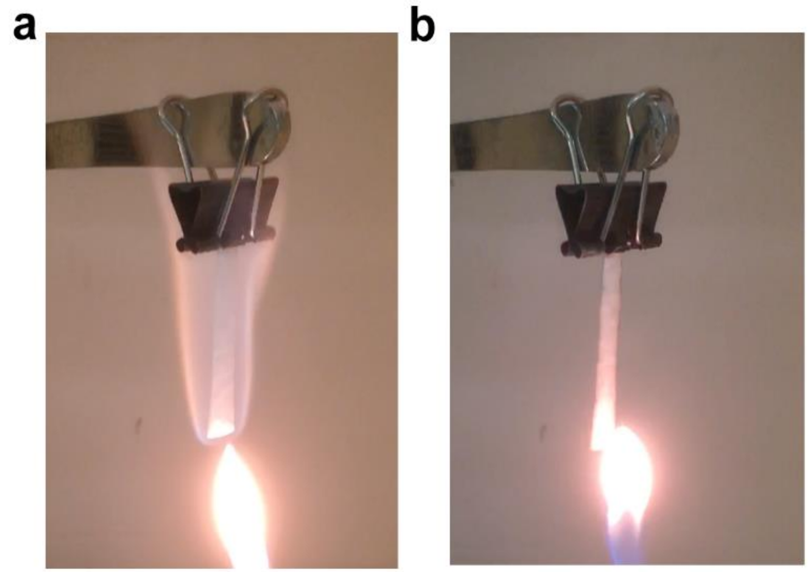
BATTERY 500 CONSORTIUM

Pacific Northwest NATIONAL LABORATORY

Technical Accomplishments

Nonflammable LHCE for high-performance LMBs





a). $LiPF_6$ in carbonates

b). EL-313

➢ High CE of LMAs and good cycle life of Li||NMC622 cells can be achieved with nonflammable EL-313.

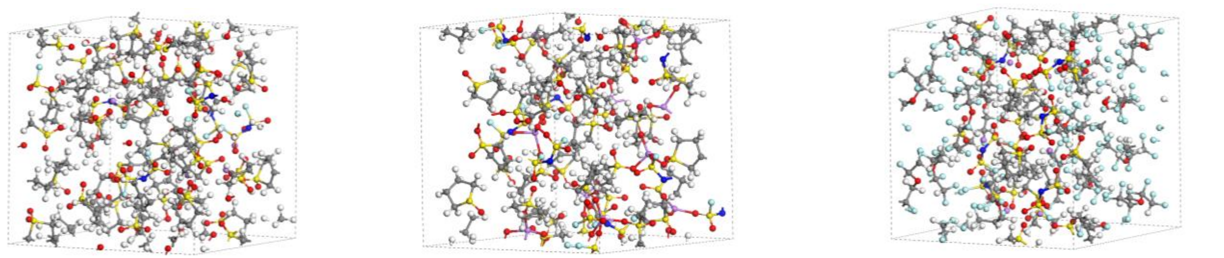
S. Chen and J. Zhang et al. Submitted for publication

Technical Accomplishments

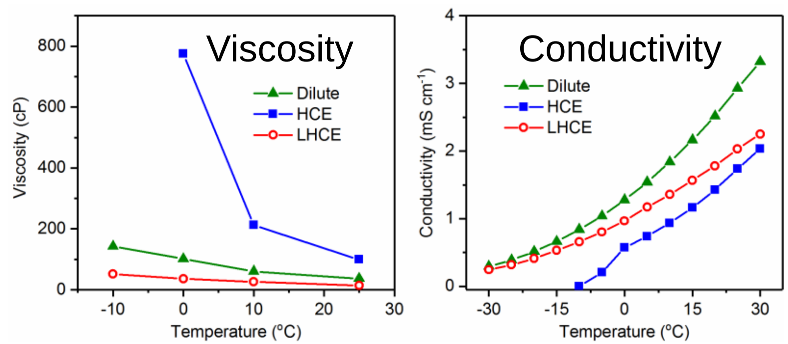
Localized high concentration electrolyte LiFSI-3TMS diluted by TTE

a. Solvation structure in HCE and is retained with addition of non-solvating TTE.

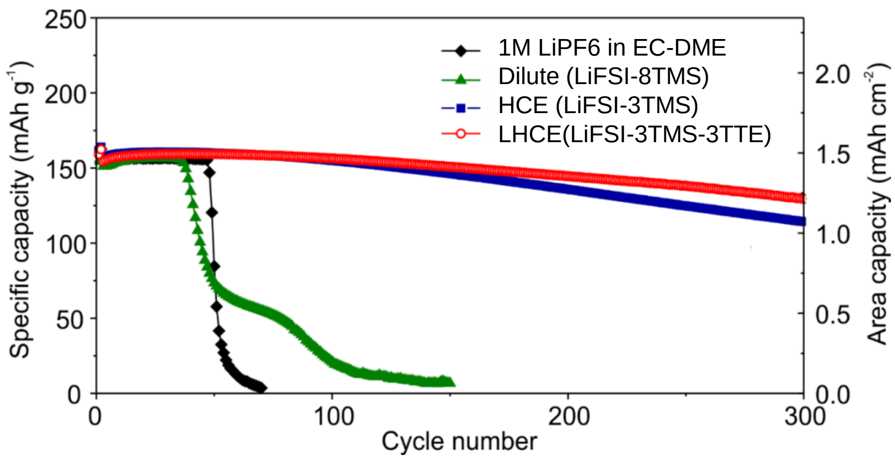
Dilute (LiFSI-8TMS) HCE (LiFSI-3TMS) LHCE(LiFSI-3TMS-3TTE)



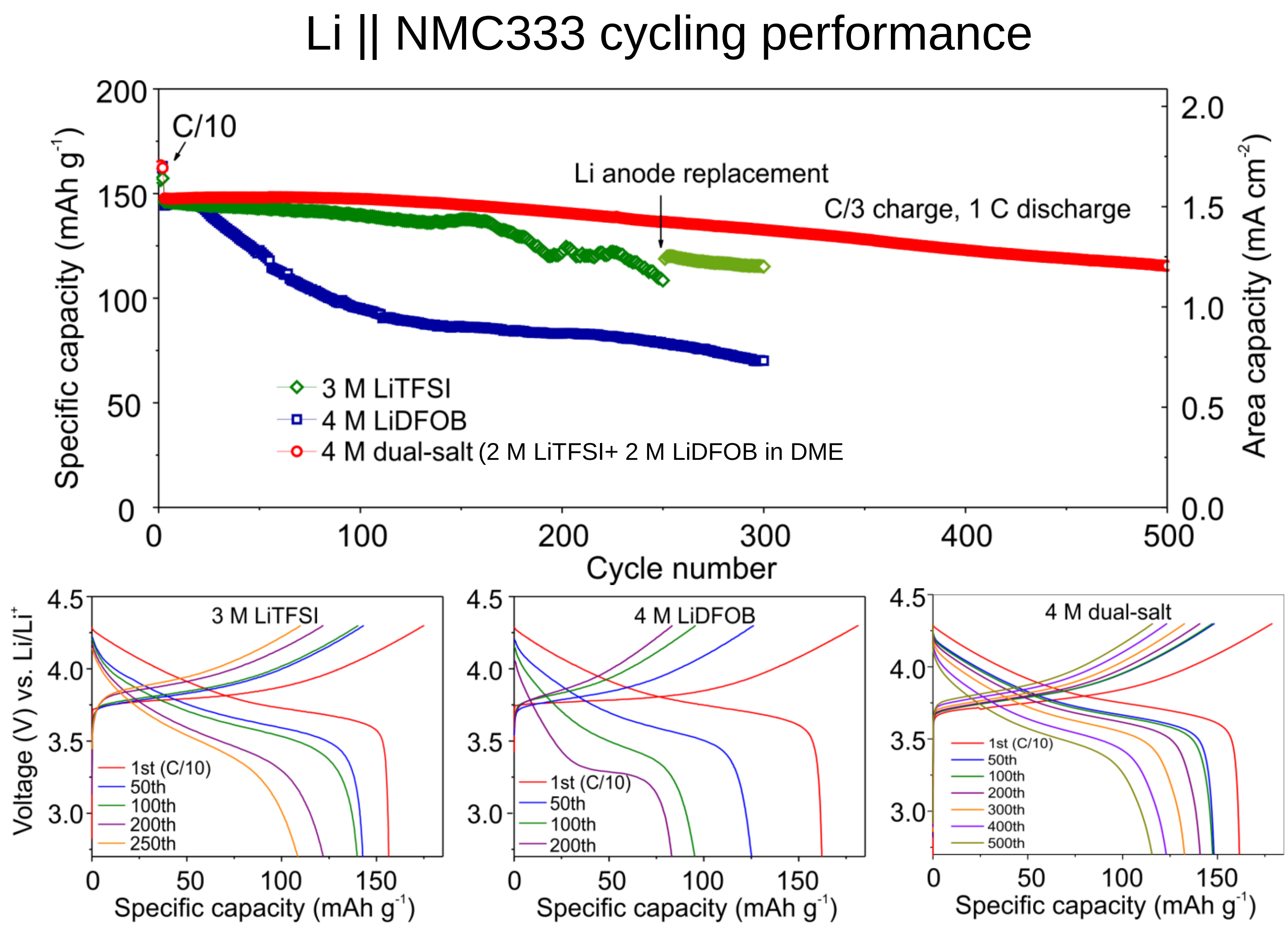
b. LHCE has a lower viscosity and higher conductivity.



c. LHCE has a lower viscosity and higher conductivity.



Technical Accomplishments

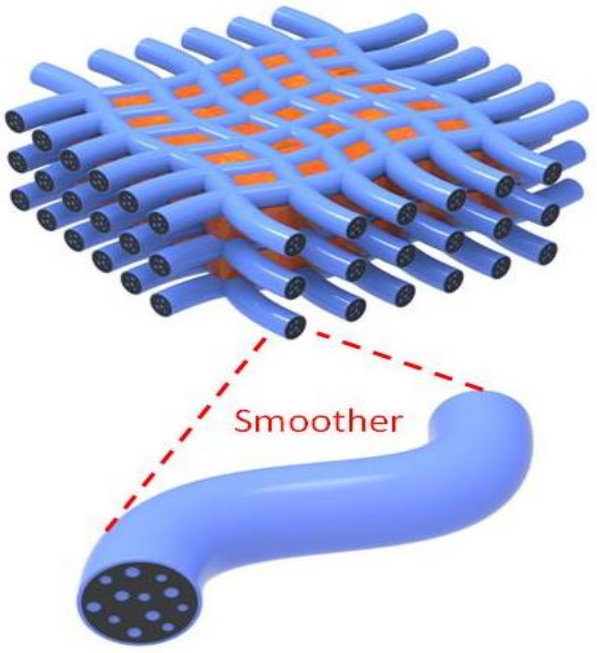


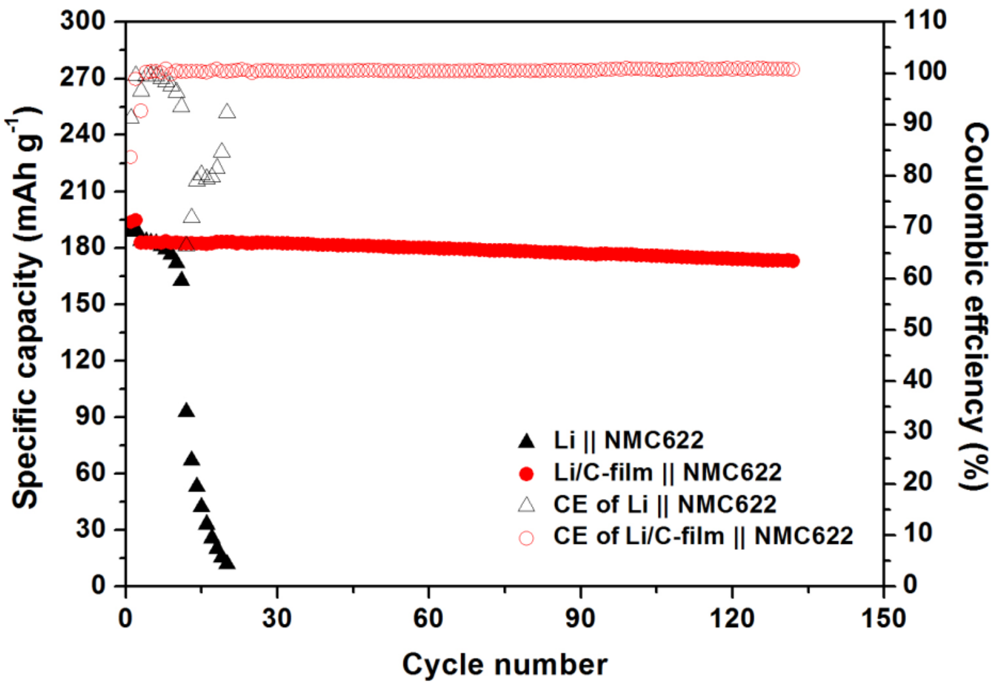
- Dual-salt ether electrolyte leads to good cycling stability of Li||NMC cells.

BATTERY 500 CONSORTIUM

Pacific Northwest NATIONAL LABORATORY

Technical Accomplishments





- ➢ Thin stable 3D architectures without sacrificing the energy density
- ➢ Controlled Li amount and low porosity
- ➢ Self-healing to prevent inhomogeneous Li metal deposition

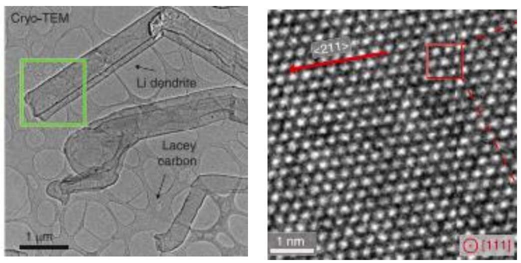

Chaojiang Niu *Jun Liu*

BATTERY 500 CONSORTIUM

Pacific Northwest NATIONAL LABORATORY

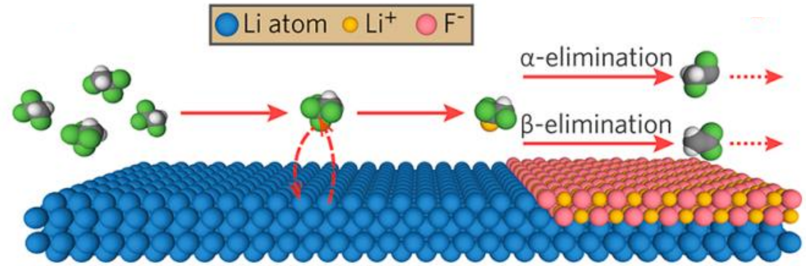
Technical Accomplishments

Reveal the atomic structure of Li metal by cryo-electron microscopy



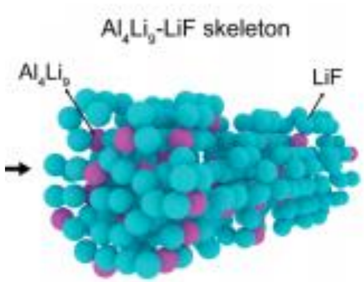
Science, 358, 506 (2017)

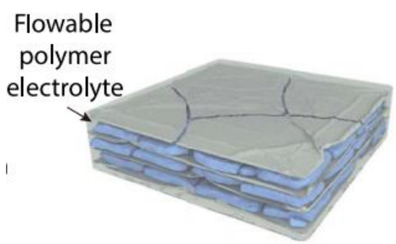
Form stable artificial SEI layer via gas-phase reaction



J. Am. Chem. Soc., **139**, 11550 (2017)
Nano Lett. **17**, 3731 (2017); *Nano Lett.* **17**, 5171 (2017); *ACS Nano* **11**, 7019 (2017)

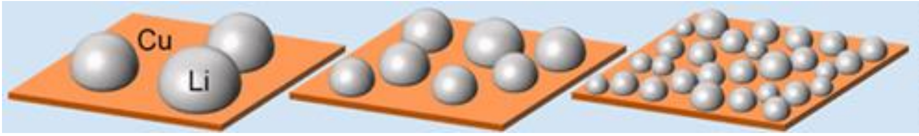
Form stable host for Li metal: Li-SiO composite





Proc. Natl. Acad. Sci., **114**, 4613 (2017)
Sci. Adv. **3,** e1701301 (2017)
Sci. Adv. **3**, eaao0713 (2017)

Selective deposition and stable encapsulation of lithium through heterogeneous seeded growth



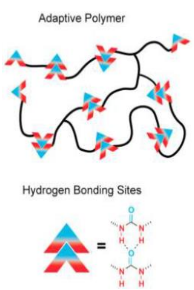
Nat. Energy **1**, 16010 (2016)
Proc. Natl. Acad. Sci., **114,** 12138 (2017)
Nano Lett. **17**, 1132 (2017)

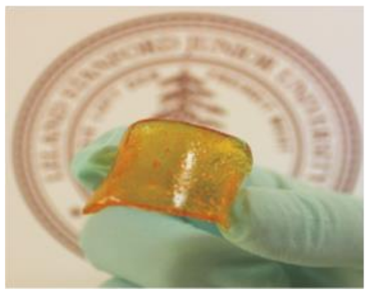
Technical Accomplishments

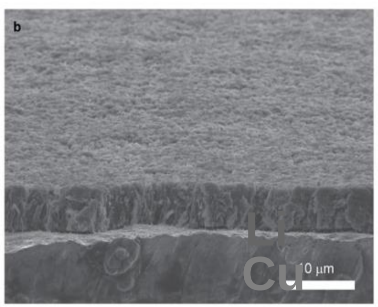
Soft, dynamic polymer coatings for Li

Self-healing polymer (SHP)

- Low glass transition temperature
- Promotes uniform Li deposition





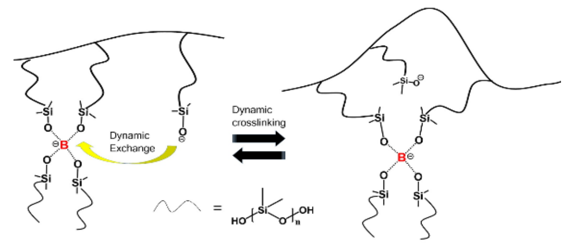


A highly viscoelastic polymer coated on Li metal anode leads to uniform Li deposition

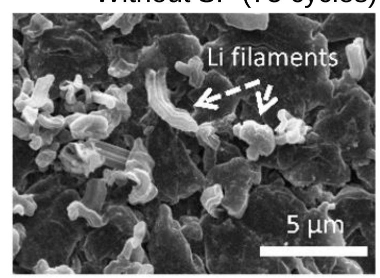
Bao, Z., Cui, Y., et al. *ACS Energy Lett.* 1247–1255 (2016)

Silly Putty (SP)

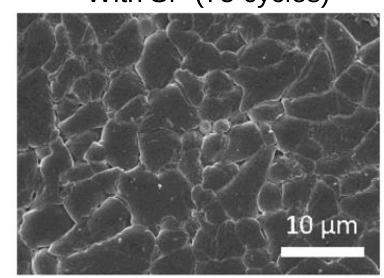
- Liquid-like at rest
- Solid-like upon stress



Without SP (75 cycles)



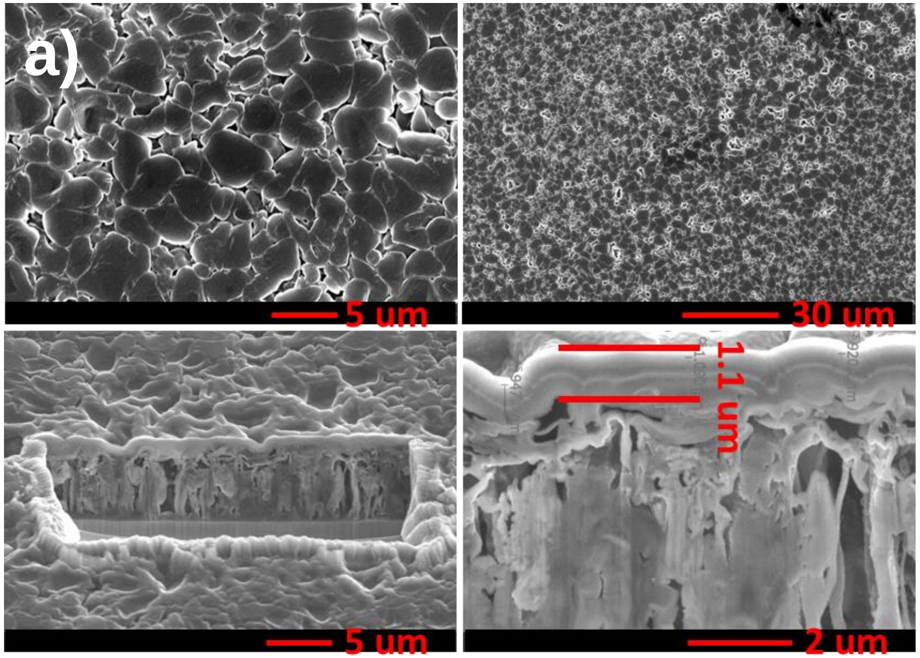
With SP (75 cycles)

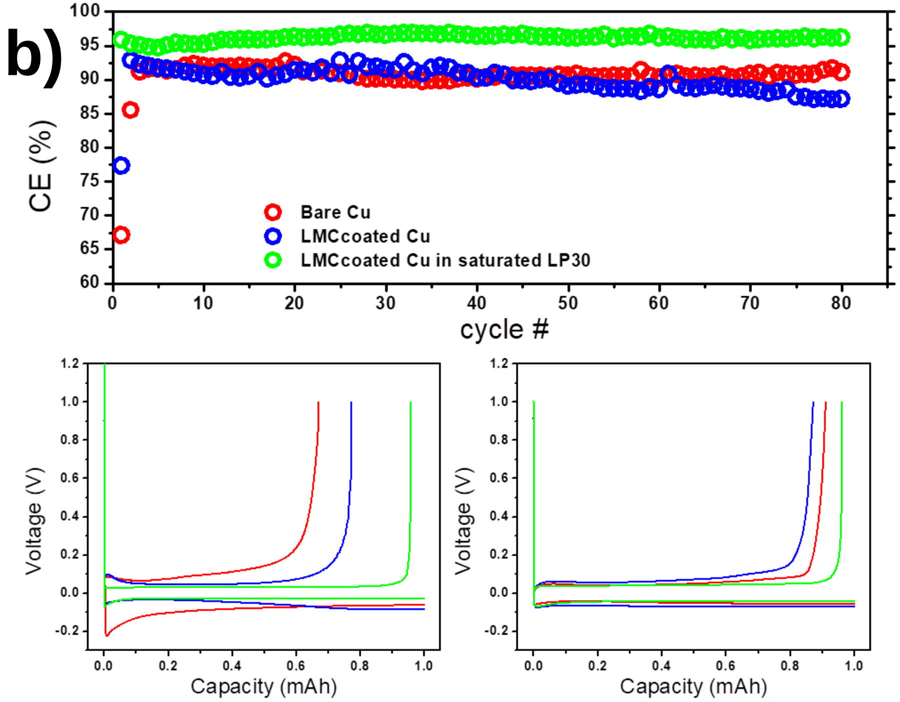


Cross-linked polymer enables adaptive interfacial layer for Li metal anodes.

Bao, Z., Cui, Y., et al. *J. Am. Chem. Soc.* 139, 4815 (2017)

Technical Accomplishments
Li-methyl Carbonate Protection Layer





- FIB-SEM shows the LMC coating layer is around 1.1 μm that covers the plated Li
- The CE of bare Cu in LP30 is 90.5%, while the CE of LMC coated Cu in LMC saturated LP30 is improved to 96.1%. LP30: 1M $LiPF_6$ in EC/DMC (1:1)

Haodong Liu, Ping Liu

UC San Diego

Collaboration and Coordination with Other Institutions

Partners:

- Stanford University: Coating and host for Li metal anode, cryo-electron microscopy
- SLAC In situ X-ray characterization of Li metal anode
- University of California at San Diego: protective coating and in situ cryo-TEM characterization
- Idaho National Laboratory: pressure effect on Li cycling and test of PNNL-made pouch cell
- University of Washington: Simulation of Li metal batteries
- UT Texas: Solid state electrolyte
- Army Research Lab: electrolyte development
- University of Maryland: electrolyte/interphase

Remaining Challenges/Barriers

To enable a Li metal batteries with more than 500 Wh/kg, new electrolytes and protection layer will be developed to enable Li metal anode to operate at the following conditions at the same time:

- CE of Li metal > 99.9%
- Lean electroltye condition (< 3g/Ah)
- Thin Li metal (N/P < 2)
- High capacity (> 4 mAh/cm2) and high current (C/3)

BATTERY 500 CONSORTIUM

Pacific Northwest NATIONAL LABORATORY

Proposed Future Work

- An fundamental understanding on the stability of Li metal anode in non-aqueous electrolyte will be developed through simulation and characterization.
- New formulation of LHCE will be developed to reduce the cost of electrolyte and improve their safety.
- Electrolyte additive or mixed solvent/mixed salts will de developed to satisfy the multiple requirement (such as high current density and lean electrolyte condition) at the same time.
- 3D conductive host will be combined with the optimized electrolytes to minimize the volume expansion of Li metal anode.
- The voltage stability of protective coating on Li metal anode will be tailored for Li/NMC cells.
- Better protection layer and/or separators will be developed to prevent Li dendrite growth in extreme conditions.

Summary

- LHCE enables high efficiency cyling of both Li metal anode (up to 99.5%) and stable cycling of Li/NMC cells (>95% capacity retention after 300 cycles and 80% capacity retention after 700 cycles in coin cells).

- Non-flammable LHCE enabled ≥300 Wh/kg Li/NMC pouch cells with more than100 stable cycles.

- Several effective protection layers, including self-healing polymer, gas induced LiF layer, Li-methyl carbonate Layer etc have been developed to enable smooth deposition of Li metal anode.

- Several stable lithium-hosts have been developed to minimize the volume expansion of Li based anode.

- Advanced characterization techniques, including cryo-electron microscopy, in situ X-Ray Diffraction and Scattering and X-Ray Absorption Spectroscopy have been developed to understand the performance of Li metal anode with unpresented accuracy and in situ capability.

BATTERY 500 CONSORTIUM

Acknowledgments

✓DOE/VTO/Battery500 program

✓PNNL Team Members: Jie Xiao, Xiaodi Ran, Lu Yu, Chaojiang Niu, Shuru Chen; Xia Cao

✓Battery 500 PIs and team members